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(54) Title: RADIATION CURABLE INKJET INKS COMPOSITIONS

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right) \quad (1)$$

(57) Abstract: A non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising: (iv) a colorant (v) a photo-initiator; and (vi) a mixture of (meth)acrylate compounds; wherein: (a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and (b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

APPLICANTS

AVECIA LIMITED

TITLE

COMPOSITIONS

COMPOSITIONS

This invention relates to radiation curable inks and to their use in ink jet printing.

Ink jet printing is a non-contact method by which droplets of ink are ejected through a fine nozzle onto a substrate. There are many demanding performance requirements for inks used in ink jet printing. For example they should provide sharp, non-feathered images having good water, solvent- light- and ozone fastness, attractive colour and high optical density. Further desirable properties for ink jet printing inks include a fast dry time (to facilitate high-speed printing), a low viscosity to enable the inks to be used in a wide range of ink jet printers, excellent mechanical resistance (to avoid the prints being rubbed off), low curl and good adhesion to a range of substrates.

Often organic solvents are included in ink jet printing inks to lower their viscosity. However such solvents can give rise to undesirable odours, particularly in the home and small, poorly ventilated offices. Inclusion of low boiling point organic solvents should be avoided in order to minimise the release of volatile organic solvents into the atmosphere. Inclusion of high boiling point solvents can increase ink dry times significantly.

US 5,270,368 discloses radiation-curable etch-resistant compositions for ink jet printing containing large proportions of monofunctional and difunctional monomers in combination with large amounts of organic solvents such as methanol to achieve a sufficiently low viscosity for jetting.

US 4,303,924 discloses radiation curable ink jet printing inks containing organic solvent and large proportions of trifunctional monomers.

WO 02/38688 discloses low viscosity radiation curable compositions which are free from solvent and have low proportions of difunctional and tri- or higher functional monomers.

According to the first aspect of the present invention there is provided a non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising:

(i) a colorant

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more

(meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1).

Preferably the value of Formula (1) is from 40 to 60, more preferably from 42.6 to 57, especially from 49 to 55.8.

The amount of colorant in the ink is preferably from 0.1 to 14%, more preferably from 1 to 10% and especially from 1.1 to 8% by weight, relative to the total weight of the ink. Preferably the colorant is not white. Preferred colorants are yellow, magenta, cyan, black, blue, indigo, violet, green, orange, red and mixtures comprising two or more thereof. Preferably the ink is free from titanium dioxide.

The colorant is preferably a dye, a pigment or a mixture thereof. More preferably the colorant is a pigment. Preferred dyes and pigments are free from ionic groups, for example disperse dyes and water-insoluble pigments are especially preferred colorants. Preferred pigments are organic or inorganic. The pigment is preferably in the form particles which are small enough to pass through the very fine nozzles used in the printheads of ink jet printers. Typically these nozzles are half the diameter of a human hair. Thus the average particle size of the pigment is preferably from 0.003 to 15 µm, more preferably from 0.004 to 5 µm and especially from 0.005 to 1µm. By choosing particles of this size advantages can be achieved in terms of storage stability for the ink and high optical density for the resultant prints. Pigment particle sizes outside these ranges may be used where printheads have particularly large nozzle diameters. Very fine dispersions of pigments and methods for their preparation are disclosed in, for example, EP 0 776 952, US 5,538,548, US 5,443,628, EP 0 259 130, US 5,285,064, EP 0 429 828 and EP 0 526 198.

Examples of inorganic pigments include carbon black, titania, iron oxide, zinc oxide and mixtures thereof. Examples of organic pigments include phthalocyanines, anthraquinones, perylenes, carbazole, monoazo and disazobenzimidazolones, isoindolinones, monoazonaphthols, diarylidepyrazolones, rhodamines, indigoids, quinacridones, diazopyranthrones, dinitranilines, pyrazolones, dianisidines, pyranthrones, tetrachloroisoindolinones, dioxazines, monoazo acrylides, anthrapyrimidines and mixtures thereof.

Examples of carbon black pigments include Regal 400R, Mogul™ L, Elftex™ 320 from Cabot Co., or Carbon Black FW18, Special Black 250, Special Black 350, Special Black 550, Printex™ 25, Printex™ 35, Printex™ 55 and Printex™ 150T from Degussa Co., and Pigment Black 7.

Further examples of pigments include C.I. Pigment Yellow 17, C.I. Pigment Blue 27. C.I. Pigment Red 49:2, C.I. Pigment Red 81:1, C.I. Pigment Red 81:3, C.I. Pigment Red 81:x, C.I. Pigment Yellow 83, C.I. Pigment Red 57:1, C.I. Pigment Red 49:1, C.I. Pigment Violet 23, C.I. Pigment Green 7, C.I. Pigment Blue 61, C.I. Pigment Red 48:1, C.I. Pigment Red 52:1, C.I. Pigment Violet 1, C.I. Pigment White 6, C.I. Pigment Blue 15, C.I. Pigment Yellow 12, C.I. Pigment Blue 56, C.I. Pigment Orange 5, C.I. Pigment Black 7, C.I. Pigment Yellow 14, C.I. Pigment Red 48:2, C.I. Pigment Blue 15:3, C.I. Pigment Yellow 1, C.I. Pigment Yellow 3, C.I. Pigment Yellow 13, C.I. Pigment Orange 16, C.I. Pigment Yellow 55, C.I. Pigment Red 41, C.I. Pigment Orange 34, C.I. Pigment Blue 62, C.I. Pigment Red 22, C.I. Pigment Red 170, C.I. Pigment Red 88, C.I. Pigment Yellow 151, C.I. Pigment Red 184, C.I. Pigment Blue 1:2, C.I. Pigment Red 3, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Red 23, C.I. Pigment Red 112, C.I. Pigment Yellow 126, C.I. Pigment Red 169, C.I. Pigment Orange 13, C.I. Pigment Red 1-10, 12, C.I. Pigment Blue 1:X, C.I. Pigment Yellow 42, C.I. Pigment Red 101, C.I. Pigment Brown 6, C.I. Pigment Brown 7, C.I. Pigment Brown 7:X, C.I. Pigment Black 11, C.I. Pigment Metal 1, C.I. Pigment Metal 2, C.I. Pigment Yellow 128, C.I. Pigment Yellow 93, C.I. Pigment Yellow 74, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 154, C.I. Pigment Yellow 185, C.I. Pigment Yellow 180, C.I. Pigment Red 122, C.I. Pigment Red 184, and bridged aluminium phthalocyanine pigments.

Further pigments are listed in *The Colour Index* and updates thereof, especially the 3rd edition, 1982, pages 6-146.

The especially preferred pigments are Pigment Yellow 128, 93, 17, 74, 138, 139, 154, 185, 180; Pigment Red 122, 57:1, 184; Pigment Blue 15:3, 15:4 and carbon black.

Preferred dyes include azo, diazo, xanthene, anthraquinone, triaryl methane, azine, thiazine, phthalocyanine and nigrosine types. Dyes may be used singly or in combination with other dyes and/or pigments. Dyes are preferably disperse or solvent soluble, examples of which may be selected from *The Colour Index* especially the 3rd edition, 1982, pages 147-263. Dyes can be metalised or non-metalised.

The ink optionally further contains a dispersant. When the colorant is a disperse dye a dispersant is often not necessary because the dye may be soluble in the formulation. Similarly when the pigment is self-dispersible (e.g. the pigment carries dispersing groups or is surface modified to be self-dispersible) no further dispersant is needed. However when the colorant is insoluble in the mixture of (meth)acrylate compounds (component (iii)) a dispersant is preferably included in the ink to assist storage stability. Suitable dispersants include, for example, polyester, polyurethane and polyacrylate dispersants, especially those in the form of high molecular weight block copolymer. Examples of dispersants include Disperbyk™ (ex BYK Chemie) and Solsperse™ (ex Avecia) dispersants. A detailed list of non-polymeric as well as some polymeric dispersants appears in, for example, *McCutcheon's Functional Materials,* North

American Edition, Manufacturing Confectioner Publishing Co., Glen Rock, N.J., pp.110-129 (1990), the entire disclosure of which is incorporated herein by reference. Dispersants suitable for use with pigments are also disclosed in DE 19636382, US 5,720,802, US 5,713,993, PCT/GB95/02501, US 5,085,689 and GB 2303376. When the ink contains a dispersant this is preferably present in an amount of 50 to 150% by weight relative to the weight of colorant.

Examples of self-dispersing pigments include surface treated carbon blacks carrying carboxy, sulphonate and/or ethylene oxide groups.

The pigment and dispersant are preferably added to the ink as a mixture. For example, a mixture of a pigment and a dispersant may be made by milling pigment in a small amount of the (meth)acrylate components c), d) and e) with a milling media, e.g. glass beads. The pigment dispersion is then typically screened and "let down" by slowly adding the remaining ink components.

The amount of photo-initiator in the ink is preferably 0.1 to 15%, more preferably 3 to 12% by weight, relative to the total weight of the ink. Preferred photo-initiators include alpha diketones, monoketals of alpha-diketones or ketoaldehydes, acyloins and their corresponding ethers, chromophore-substituted halo-s-triazines, and chromophore-substituted halomethyl-oxadiozoles. Specific examples of photo-initiators include acetophenone, propiophenone, 2-phenyl-acetophenone, 2-chloro-2-phenyl-acetophenone, 2-2-dichloro-2-phenyl-acetophenone, 2-butoxy-2-phenyl acetophenone, 2,2-dimethoxy-2-phenyl-acetophenone, 2,2-diethoxy-acetophenone, 2-methylol-2-methoxy-2-phenyl-acetophenone, benzophenone, 4-trichloromethyl benzophenone, indenone, 1-3-indanedione, fluorenone, xanthone, thioxanthone, 2-chlorothioxanthone, anthraquinone, 2-ethylanthraquinone, biacetyl, glyoxal, 1,2-indanedione, p-chlorophenyl-glyoxal, benzil, camphoquinone, and benzoin methyl and ethyl esters. Commercial photo-initiators particularly suitable for use in the present invention include Speedcure™ ITX, and Irgacure™ 369. The ink optionally further contains one or more co-initiators or amine synergists in order to improve cure rate. Examples include isopropylthioxanthone, ethyl-4-(dimethylamine) benzoate, 2-ethyl hexyl dimethylaminobenzoate and dimethylaminoethyl methacrylate.

Preferably the photo-initiator is other than a cationic photo-initiator. Preferably the photo-initiator is a free radical photo-initiator.

Preferably the photo-initiator is soluble in the ink.

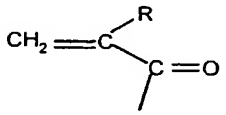
A single photo-initiator may be used although it is preferable that the photo-initiator is a mixture of two or more photo-initiators because this can lead to a broader spectral response, improved depth of cure and improved cure rate with opacifying pigments such as carbon black.

Preferably the ink further comprises a stabiliser to improve the storage stability of the ink and prevent premature curing. The stabiliser is preferably an antioxidant, a radical trap, a radical quencher or the like, e.g. a phenol, thiol, quinone, hydroquinone, amine,

xanthate or an N-alkyl or N-aryl aniline. Too much stabiliser will prevent cure entirely. Hence preferred amounts of stabiliser are from 0 to 10%, more preferably from 0.01 to 5%, and especially from 0.1 to 3% by weight relative to the total weight of the ink. Mixtures of stabilisers are preferable for the best ink storage lifetime.

Preferably the ink is curable by actinic radiation or particle beam, especially by UV or electron beam radiation.

Mono (meth)acrylate compounds have one (and only one) acrylate or methacrylate group. This group is, as is known in the art, is polymerisable when irradiated in the presence of a photo-initiator. (Meth)acrylate groups are represented by the formula:



wherein R is H or methyl

The mono (meth)acrylate compound is preferably a monomer. Examples mono (meth)acrylate monomers include cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl (meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate. Preferred mono (meth)acrylate monomers include lauryl (meth)acrylate, tetrahydro furfuryl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, iso-octyl (meth)acrylate, iso-decyl (meth)acrylate, tridecyl (meth)acrylate, dodecyl (meth)acrylate, isobornyl (meth)acrylate, cyclic trimethylol propane formal (meth)acrylate.

It is especially preferred that the one or more monomer (meth)acrylate compounds is or comprises isobornyl acrylate.

Di (meth)acrylate compounds have two (and only two) groups selected from acrylate and methacrylate.

Preferred di (meth)acrylate compounds are di (meth)acrylate monomers, for example di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy

ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol.

It is especially preferred that the one or more di(meth)acrylate compounds is or comprises 1,6 hexane diol diacrylate.

The compound(s) having three or more (meth) acrylate groups have three or more groups selected from acrylate and methacrylate. The compound having three or more (meth)acrylate groups is preferably a monomer, oligomer or polymer, preferred examples of which include trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics.

It is especially preferred that the one or more compounds comprising three or more (meth)acrylate groups is or comprises trimethylol propane triacrylate and/or ethoxylated trimethylol propane triacrylate.

Inks which contain acrylates polymerise more quickly than those containing methacrylates when exposed to actinic or particle beam radiation. Consequently, the amount of methacrylate is preferably not greater than 20%, more preferably not greater than 10% and especially not greater than 5% of component (iii). It is particularly preferred that component (iii) contains no methacrylate.

Optionally the ink further comprises a polymer or oligomer containing no (meth)acrylate groups. Preferably the polymer and oligomer containing no (meth)acrylate groups is present in the ink at from 0 to15%, more preferably from 0 to 10% and most preferably from 0 to 5% by weight relative to the total weight of the ink.

Inks of the present invention are substantially solvent free. That is to say no solvent or water is present in the ink except for trace amounts which may be present as impurities in any of the ink components. Preferably any such residues are less than 2%, more preferably less than 0.5% and especially less than 0.01% by weight relative to the total weight of ink. As hereinbefore described inks of the present invention are particularly suitable for use in ink jet printing. A preferred ink jet type for inks of the present invention is piezo ink jet printing.

The viscosity of the inks of the present invention are preferably 1 to 30 mPa.s, more preferably from 2 to 25 mPa.s at 60°C. The ink composition may optionally have a higher viscosity at room temperature provided that the final ink meets the above viscosity requirements at the above temperature.

The surface tension of the ink of the present invention is preferably below 40 dynes/cm.

Inks of the present invention are preferably free from particulate impurities that would tend to block an ink jet nozzle. To achieve this the ink is preferably filtered through a filter with a pore size of less than 10μm, more preferably less than 3μm and especially less than 1μm.

A particularly preferred ink according to the invention is a non-aqueous, substantially solvent-free, radiation curable ink having a viscosity of 1 to 30m Pa.s at 60°C comprising:

(i) a yellow, magenta, cyan, black, blue, indigo, violet, green, orange or red pigment or a mixture comprising two or more thereof;

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the pigment is present in the ink an amount of from 1.1 to 8% by weight relative to the total weight of ink;

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is from 40 to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1)

(c) the photo-initiator is present in the ink in an amount of 3 to 12% by weight relative to the total weight of ink;

(d) the one or more mono (meth)acrylate compounds are selected from the group consisting of cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl

(meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate and mixtures thereof;

(e) the one or more di (meth)acrylate compounds are selected from the group consisting of di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol and mixtures thereof; and

(f) the one or more compounds having three or more (meth)acrylate groups are selected from the group consisting of trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics and mixtures thereof.

In this preferred ink the mixture of (meth)acrylate compounds is preferably present in the ink in an amount of from 70 to 95.9%, more preferably from 75 to 95.9%, and especially from 78 to 95.9% by weight relative to the total weight of ink. Any difference between the weight of components (i), (ii) and (iii) and 100% is made up by other customary ink additives, e.g. flow control agents, dispersants, biocides, rheology modifiers and so on other than water or organic solvent.

Inks of the present invention may contain further components in addition to components (i) to (iii) specified above, for example preservatives, biocides, rheology modifiers, surfactants, levelling agents, antifoaming agents, anti-kogation agents and combinations thereof.

According to a second aspect of the present invention there is provided a process for printing an image onto a substrate comprising applying thereto an ink according to the first aspect of the present invention by means of an ink jet printer and curing the ink, preferably using an electron beam or more preferably using ultra violet light. Printed substrates obtained by this process form a further feature of the present invention.

Preferred substrates are metal, plastic, ceramic, glass, wood, printed circuit boards and plain and coated papers. Preferred applications include printing for home/office use, packaging, labelling and barcodes, particularly wide format graphics, printed circuit board manufacture, signage, wall coverings and decorative laminates.

According to a third aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and an ink wherein the ink is present in the chamber and is as defined in the first aspect of the invention.

The invention in further illustrated by the following examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

A radiation curable ink was prepared containing the following components:

Component	Weight (g)	Type
Sartomer™ 256	10.02	Monoacrylate
Sartomer™ 238	10.02	Diacrylate
Sartomer™ 351	40.07	Triacrylate
Regal ™250R	1.75	Pigment
Solsperse™ 32000	1.09	Dispersant
Solsperse™ 5000	0.06	Dispersant
Irgacure™ 369	2.80	Photo-initiator
Speedcure™ EHA	2.80	Amine Synergist
Speedcure™ ITX	1.40	Photo-initiator

The procedure for preparation of the above ink was as follows:

A millbase was prepared by bead milling Regal™ 250R pigment with a small amount of Sartomer™ 256 and Sartomer™ 238 together with Solsperse™ 32000 and 5000 dispersants until a fine particle dispersion was formed. The remaining components were then added in the dark and the mixture was homogenised and then filtered through a 1 micron Whatman™ syringe filter.

The percentages of mono acrylate (16.7%), di acrylate (16.7%) and tri acrylate (66.6%) compounds by weight relative to the total weight of such compounds (100%) are such that the value of Formula (1) was (16.7 + 0.628 X (16.7/sin 60 + 66.6/tan60) = 52.93.

Comparative Example 1

A radiation curable ink was prepared (in an analogous manner to Example 1) containing the following components:

Component	Weight (g)	Type
Sartomer™ 256	39.55	Monoacrylate
Sartomer™ 238	9.89	Diacrylate
Sartomer™ 351	9.89	Triacrylate
Regal™ 250R	1.73	Pigment
Solsperse™ 32000	1.08	Dispersant
Solsperse™ 5000	0.06	Dispersant
Irgacure™ 369	2.76	Photo-initiator
Speedcure™ EHA	2.76	Amine Synergist
Speedcure™ ITX	1.38	Photo-initiator

The percentages of mono acrylate , di acrylate and tri acrylate compounds by weight relative to the total weight of such compounds are such that the value of Formula (1) was 84.79.

Results

The inks describe in Example 1 and Comparative Example 1 were each coated onto sheen cards using an 8μm K-bar coater. The coatings were cured using Fusion Systems apparatus fitted with a "D" 300W/inch bulb using cure energy in the range UV_A 0.37 – 0.74, UV_B 0.172 – 0.99 and UV_C 0.07 – 0.11 at belt/cure speeds of 25M/min or 15M/min.

The Reflectance Optical Density (ROD) of the cured coated sheen cards was measured using an XRite 938 Spectrodensitometer using density status T, illuminant D50 and 2° observer.

The Chemical Resistance (% loss) was determined by performing 5 x MEK (methyl ethyl ketone) double rubs on the coated cured sheen cards and then measuring the ROD in the rubbed region. The Chemical Resistance (% loss) value was then expressed via

$$\text{Chemical Resistance (\% loss)} = 100\ \frac{(\text{ROD Initial} - \text{ROD after 5 x MEK rubs})}{\text{ROD Initial}}$$

Hence small values of Chemical Resistance (% loss) represent higher solvent resistance.

The viscosity was measured by using a Brookfield viscometer at 50°C operating at 100 revolutions per minute and using a UL spindle

The surface tension of the inks were determined at 25°C using a Kruss Surface Tension Balance.

The hardness of the print was assessed in the conventional manner using pencils of different hardness, where the hardness is determined as the lowest hardness value that forms a scratch in the print.

Property	Example 1	Comparative Example 1
ROD	1.821	1.668
Chemical Resistance (% loss)	1.7	29.2
Viscosity (@ 50°C) mPa.s	11.5	4.32
Surface Tension (@ 25°C) dynes/cm	37	37
Pencil Hardness	4H	6B
Belt Cure Speed	25	15

The above table shows that the ink of Example 1 has better chemical resistance and a faster cure speed than Comparative Example 1 whilst still retaining a low viscosity suitable for ink jet printing. Furthermore, Example 1 has better pencil hardness and a higher ROD than Comparative Example 1. The ink described in Example 1 was readily jetted through a Spectra Galaxy printhead.

Further inks of the present invention were prepared (in an analogous manner to Example 1) containing:

Ingredient		Yellow %	Magenta %	Cyan %	Black %
Sartomer™ 506	Isobornyl acrylate	8.73	8.18	8.58	8.57
Sartomer™ SR238	1,6 hexanediol diacrylate	22.48	30.84	25.42	22.74
Sartomer™ 306	tripropyleneglycol diacrylate	3.7	5.95	2.97	4.18
Sartomer™ SR351	trimethylolpropane triacrylate	34.9	24.53	32.54	33.48
Sartomer™ SR454	Ethoxylated trimethylolpropane triacrylate	17.45	12.26	16.28	16.74
Tegorad™ 2100	ST modifier (silicone acrylate)	0.15	0.15	0.15	0.15
Irgacure™ 369	Photo-initiator	4	4	4	4
Speedcure™ EHA	Amine Synergist	4	4	4	4
Speedcure™ ITX	Photo-initiator	2	2	2	2
Paliotol™ Yellow D1819	Pigment	2	0	0	0
Hostaperm™ Red E5B02	Pigment	0	5	0	0
Irgalite™ Blue GLVO	Pigment	0	0	2.5	0
Regal™ 250	Pigment	0	0	0	2.5
Solsperse™ 32000	Dispersant	0.6	3	1.5	1.56
Solsperse™ 5000	Dispersant	0	0.1	0.05	0.09

Such inks showed excellent printing performance through a Spectra Galaxy printhead and had very good chemical resistance.

CLAIMS

1. A non-aqueous, substantially solvent-free, radiation curable ink having a viscosity less than 30m Pa.s at 60°C, comprising:

(i) a colorant

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the colorant is present in the ink in an amount of 0.1 to 14.9% by weight relative to the total weight of ink; and

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is less than or equal to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1).

2. An ink according to claim 1 wherein the colorant is a pigment.

3. An ink according to any one of the preceding claims wherein the mono (meth)acrylate compounds and di (meth)acrylate compounds are monomers.

4. An ink according to any one of the preceding claims wherein the value of Formula (1) is from 49 to 55.8.

5. An ink according to any one of the preceding claims wherein the photo-initiator is a free radical photo-initiator.

6. An ink according to any one of the preceding claims wherein the one or more mono (meth)acrylate compounds is or comprises isobornyl acrylate.

7. An ink according to any one of the preceding claims wherein the one or more di (meth)acrylate compounds is or comprises 1,6 hexanediol diacrylate.

8. An ink according to any one of the preceding claims wherein the one or more compound comprising three or more (meth)acrylate groups is or comprises trimethylolpropane triacrylate and/or ethoxylated trimethylolpropane triacrylate.

9. An ink according to any one of the preceding claims which further comprises a dispersant and/or an amine synergist.

10. An ink according to any one of the preceding claims wherein the colorant is present in an amount of 1.1 to 8% by weight, relative to the total weight of the ink.

11. An ink according to any one of the preceding claims wherein the colorant is not white.

12. An ink according to any one of the preceding claims which is free from titanium dioxide.

13. An ink according to any one of the preceding claims wherein the photo-initiator is present in an amount of 3 to 12 % by weight, relative to the total weight of the ink.

14. An ink according to claim 1 comprising:

(i) a yellow, magenta, cyan, black, blue, indigo, violet, green, orange or red pigment or a mixture comprising two or more thereof;

(ii) a photo-initiator; and

(iii) a mixture of (meth)acrylate compounds;

wherein:

(a) the pigment is present in the ink an amount of from 1.1 to 8% by weight relative to the total weight of ink;

(b) the mixture of (meth)acrylate compounds comprises c% of one or more mono (meth)acrylate compounds, d% of one or more di (meth)acrylate compounds and e% of one or more compounds having three or more (meth)acrylate groups, wherein the values of c%, d% and e% are by weight relative to the total weight of the mono (meth)acrylate compounds, di (meth)acrylate compounds and compounds having three or more (meth)acrylate groups and are such that the value of Formula (1) is from 40 to 60:

$$c\% + 0.628\left(\frac{d\%}{\sin 60} + \frac{e\%}{\tan 60}\right)$$

Formula (1)

(c) the photo-initiator is present in the ink in an amount of 3 to 12% by weight relative to the total weight of ink;

(d) the one or more mono (meth)acrylate compounds are selected from the group consisting of cyclic trimethylolpropane formal (meth)acrylate, ethoxylated tetra hydrofurfuryl (meth)acrylate, phenoxy ethyl (meth)acrylate, trimethylol propane formal (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, monomethoxy neopentyl glycol propoxylate mono (meth)acrylate, monomethoxy tripropylene glycol mono (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, iso-decyl (meth)acrylate, iso-octyl (meth)acrylate, iso-nonyl (meth)acrylate, tridecyl (meth)acrylate, iso-bornyl (meth)acrylate, ethoxyl nonyl phenol (meth)acrylate, ethoxylated phenol (meth)acrylate, 2-hydroxyl ethyl (meth) acrylate, 4-hydroxyl butyl (meth) acrylate, 2-hydroxy propyl (meth) acrylate, iso-butyl (meth) acrylate, tert-butyl (meth) acrylate, cetyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl hexyl (meth)acrylate, 2-dimethyl amino ethyl (meth) acrylate, trifluoro ethyl (meth)acrylate, 3-methoxy butyl (meth)acrylate, dicyclopentenyl (meth)acrylate, polyethylene glycol mono (meth)acrylate and poly propylene glycol mono (meth)acrylate and mixtures thereof;

(e) the one or more di (meth)acrylate compounds are selected from the group consisting of di(meth)acrylates of 1,4 butane diol, 1-6 hexane diol, neopentyl glycol, mono, di, tri and poly ethylene glycols, mono, di, tri and poly propylene glycols, mono methoxy ethoxylated trimethylolpropane, propoxylated neopentyl glycol, ethoxylated neopentyl glycol, 1,2 butylene glycol and ethoxylated hexane diol and mixtures thereof; and

(f) the one or more compounds having three or more (meth)acrylate groups are selected from the group consisting of trimethylol propane tri(meth)acrylate, ethoxylated trimethylol propane tri(meth)acrylate, propoxylated trimethylol propane tri(meth)acrylate, glycerol tri(meth)acrylate, propoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ditrimethylol propane tetra (meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, ethoxylated di-pentaerylthritol tetra (meth)acrylate, tetra methylol methane tetra (meth)acrylate, multifunctional (meth)acrylate-urethanes, (meth)acrylate-polyesters and (meth)acrylate acrylics and mixtures thereof.

15. An ink according to any one of the preceding claims which has been filtered through a filter having a mean pore size of less than 10μm.

16. An ink according to any one of the preceding claims for use in ink jet printing.

17. A process for printing an image onto a substrate comprising printing an image onto a substrate using an ink according to any one of the preceding claims by means of an ink jet printer and curing the ink.

18. A process according to claim 17 wherein the curing is performed using an electron beam or ultra violet light.

19. A printed substrate obtained by the process of claim 17 or 18.

20. An ink jet printer cartridge comprising a chamber and an ink wherein the ink is present in the chamber and is as defined in one of claims 1 to 16.

21. A substrate printed with an image using an ink according to any one of the claims 1 to 16.

22. A substrate printed with an image by a process according to claim 17 or 18.

INTERNATIONAL SEARCH REPORT

Int[redacted]ional Application No
PCT/GB 03/03836

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/10 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 29788 A (JOHNSON STEVE ;XAAR TECH LTD (GB); WOODS JILL (GB)) 17 June 1999 (1999-06-17) page 3, paragraph 1 -page 4, paragraph 1 page 5, paragraph 4 -page 8, paragraph 3 page 9, paragraph 2 -page 12, paragraph 1 page 16, paragraph 1 -page 17, line 7 page 17, paragraph 2 -page 18, paragraph 1 page 21, paragraph 2; examples 1,2 ---	1-22
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 99 29787 A (JOHNSON STEVE ;XAAR TECH LTD (GB); WOODS JILL (GB)) 17 June 1999 (1999-06-17) page 3, paragraphs 1,2 page 5, paragraph 3 -page 8, line 3 page 8, paragraph 2 -page 11, paragraph 1 page 15, paragraph 2 -page 17, paragraph 1 page 17, paragraph 3 -page 18, paragraph 1 page 19, paragraph 2 page 21, paragraph 3; table 1	1-10, 13-22
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